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**CORROSION RESISTANCE OF ZIRCONIUM AND ITS ALLOYS
IN WATER AND STEAM AT HIGH TEMPERATURES**

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Due to their nuclear, physical, chemical and engineering properties zirconium and its alloys have a number of advantages in comparison with other structural materials. However when zirconium and its alloys are used in reactors cooled by water or steam these advantages severely decrease due to hydrogen absorption which leads to deterioration of their corrosive and mechanical properties.

The mechanism of effect of additions and alloying elements in zirconium on its corrosion resistance in water and steam has been studied insufficiently (1,2).

Some investigations on the processes of zirconium and its alloys corrosion were carried out by the authors earlier. The paper (3) describes the studies of oxidation kinetics of zirconium and its alloys, of structure and composition of the resulting oxide films. The paper (4) was devoted to studies of zirconium alloying effect on protective properties and critical thickness of oxide film appearing on it. This paper describes the results of further investigation carried out for studying the redistribution of some impurities and alloying elements in zirconium after the corrosion in water and steam at high conditions. The oxide film appearing as a result of the corrosion was also studied with an electron microscope.

Methods and objects of research

The redistribution of additions was studied with the help of radioactive isotopes. Two methods were used. In the first case the radioactive isotopes were introduced into zirconium during the alloying process. The specimens were heat treated

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and then subjected to corrosion tests. The redistribution of impurities and alloys in the corrosion process in the inactive water and steam of high parameters was investigated. In the second method the inactive alloys of zirconium in water and steam medium containing tritium were investigated. The specimens were activated during the corrosion process due to interaction of tritium in water with zirconium.

Using the electron microscope EM-5 the topography of the surface was studied after corrosion as well as the structure of the generated films.

In order to investigate the redistribution of elements in the corrosion process, zirconium alloys with radioactive isotopes of carbon, nickel and iron (see table I) were smelted.

The cast alloys were heat-forged in air at 900-700°. The samples were made in the form of 1 x 8 x 20 mm rectangles. After heat treatment the samples were studied autoradiographically and metallographically.

Corrosion experiments were carried out in static conditions in microautoclaves filled with distilled water at 370-400°C and at the pressure corresponding to the elasticity of water vapour at the given temperature. The time of the experiment was limited by the appearance of a white oxide film. With some alloys this white film was not observed, but the experimental time did not exceed 1000 hours.

After corrosion experiments a series of unparallel cuts at an angle of about 1° were made in order to investigate the redistribution of the elements in the oxide film as well as in the metal. These cuts were made by means of grinding and polishing.

In order to determine the effect of hydrogen on the corrosion resistance of zirconium and its alloys, experiments were carried in the vapour of tritium water with a radioactivity of 1 curie/ml. Investigations of an iodide zirconium, zirconium alloys with 0.7% Fe and 0.7% Ni and of zirconium with nitrogen content of 0.025 weight percent were made. The experiments were carried in static conditions at the temperature of 400°C and under the

pressure of 220 atm. The maximum time of experiment was 750 hours.

The analysis of the samples after the corrosion experiments in tritium water was also carried on the unparallel cuts by the metallographic and autoradiographic methods.

Experimental results

The influence of carbon

The distribution of carbon in zirconium depends upon the heat treatment of the alloys, as our investigations have proved /5,6/. In order to investigate the influence of the carbon distribution upon the corrosion resistance of zirconium, the heat treatment of the samples before the corrosion experiments was carried under several conditions (table I). They resulted in a different distribution of carbon in zirconium samples. This was observed on the boundaries and subboundaries of the α -phase, which appeared at the $\beta \rightarrow \alpha$ transformation (hardening and annealing at 1000°); the uniform distribution of carbon in α - solid zirconium solution (annealing at 800°) was also observed.

Corrosion experiments according to the conditions given in table I, showed that all the samples, irrespective of the heat treatment conditions had a low corrosion resistance and were covered with a white crumbling film after 125 hours. Under this film there was a dark transitional layer which lay tightly on the metal.

Fig. I and 2 show autoradiograms of unparallel cuts of the zirconium-carbon samples, showing the distribution of carbon in the surface film, the transitional layer and inside the sample. The carbon distribution in zirconium remained the same after the experiment as it was before the experiment, provided no corrosion occurred in the samples. The autoradiograms show that corrosion begins at the boundaries of the grains of the α -phase and then spreads along the whole volume (fig. I). In samples which were subjected to the heat treatment at high temperature in the region of β -phase, the corrosion process is observed at first at the boundaries and subboundaries of the grains. This is caused by allotropical transformation of $\beta \rightarrow \alpha$ phase, then the pro-

cess spreads over the grain volume (fig.2). During the corrosion process a partial decarbonization of zirconium takes place.

Fig.3 shows autoradiograms from the same surface of the sample annealed at 1000° before and after corrosion. It is apparent that after corrosion the degree of decarbonization and hence the degree of corrosion is different for various grains. This can be proved by a different relative darkening of parts in the autoradiograms, corresponding to single zirconium grains. This is apparently connected with different orientation of the zirconium grains to the surface of the sample. Differently orientated grains of zirconium corrode at different rate, which can probably be explained by the anisotropy of the oxygen diffusion into the lattice of α -zirconium.

A radiometric analysis of unparallel cuts of zirconium samples after corrosion has been carried out using the technique described in the paper (7,8). According to the data of the radiometric analysis and those measured by a microphotometer the content of carbon in the surface film is 0.3 compared with that of the original content in zirconium. This shows that decarbonization of zirconium takes place during the corrosion process and it may be connected with the generation and removal of carbon oxides. Nevertheless a part of carbon still remains in the oxide film.

The effect of alloying impurities

We have shown that alloying in the range of zirconium solubility with tin increases the energy of self-diffusion activation (5), increases the sublimation heat (9), decreases the effect of structural factor on diffusion (10), and attenuates the decrease of normal elasticity model with temperature rise. Thus tin alloying improves the strength characteristics at higher temperatures. This may be connected with a sufficient decrease of excessive concentration of vacancies. The effect of niobium resembles that of tin (5, 10).

In addition tin neutralizes the harmful effect of nitrogen on corrosion properties of zirconium. The iron, nickel and

chromium impurities form insoluble intermetalides (Fe_2Zr , Zr_2Ni and Cr_2Zr); which being microcathode areas anodically polarize the zirconium matrix and facilitate the formation of a thin oxide film with a higher strength (II).

The distribution of carbon in zirconium alloys with 0.05 per cent radioactive carbon and 1 W per cent of tin depends upon the heat treatment. After hardening and annealing in β -area, one can observe a subboundary and boundary concentration of carbon. The annealing in the α -area leads to a nearly uniform distribution of carbon in the alloy. After the corrosion experiments during 580 hours the surface of the samples were satisfactory. Distribution of carbon in the surface film and inter the sample was the same and did not change comparing to the original distribution of carbon in the alloy.

Zirconium alloy with 0.1 W per cent of tin was tested at a higher temperature of water and already after 125 hours it was covered with a white film. No visible changes in the distribution of carbon in the film and inside the sample were observed. Like in the previous alloy the reduction of carbon content in the surface film compared to that inside the sample is observed. According to the radiometric analysis and to the microphotometering of the autoradiograms the carbon content in the film compared to that of the original was 0.4.

The zirconium alloys with 0.1 W per cent of carbon and 1 W per cent of niobium, 0.8 W per cent of iron and 0.8 W per cent of nickel were tested after annealing at 750° during 1 hour. In all alloys carbon after the heat treatment was distributed in α -solid solution and in the form of carbides. The distribution of carbon in the surface film and inside the metal were alike. The regions of the autoradiogram over the film are of a lighter colour than over the inner parts of the sample. Microphotom

etering of the autoradiograms of the unparallel cuts of the samples showed that the carbon content in the film as compared to the initial contents in the sample was - 0.5 for zirconium alloyed with 0.1 W carbon and 1 W niobium and - 0.6 for zirconium alloyed with 0.1 W carbon and 0.8 W nickel.

The redistribution of nickel after corrosion tests in hot water was studied in the zirconium alloy with 0.6 W nickel and in triple zirconium alloy with 0.6 W iron and 0.4 W nickel.

The autoradiograms of the unparallel cuts of the samples annealed before the tests at 1000° show three layers (fig.4). In the lighter surface layer, separate grains of high temperature phase of the alloy are present; these differ in the degree of darkening. Then comes the transitional layer, where the character of the distribution is the same as inside the sample, but the intensity of darkening is weaker. In the third layer the character of the nickel distribution is the same as in the original sample. The microstructure of the transitional layer (fig.4) shows a deeper corrosion of the subboundary of α -phase.

After hardening at 1000° the zirconium alloy with 0.6 W nickel had a coarse-grained structure. The autoradiograms of the unparallel cuts of the samples, hardened at 1000° before the test do not show any nickel redistribution inside the sample. Selective corrosion in the transitional layer was not observed in the microstructure.

The autoradiogram of the unparallel cut of the zirconium sample with 0.6 W nickel annealed before the test at 750° does not show any nickel redistribution in the corrosion process. But the microstructure of the transitional layer shows selective corrosion along the subboundaries of the grains, where the nickel segregations are concentrated (fig.5).

The zirconium alloy with 0.4 W radioactive nickel and 0.6 W iron was heat treated in α - and β -regions; this resulted in different nickel distribution. After annealing at 800° there appeared a stabilised α -phase, which was surrounded at the grain boundaries with rather coarse segregations of intermetallics Zr_2Ni and Fe_2Zr . They concentrated all the nickel and iron. After hardening at 1000° one part of nickel and iron remains in the solid α -zirconium solution, while another part is concentrated along the boundaries and subboundaries of the α -phase grains having a needle structure. After annealing at 1000° and 750° the segregation of nickel and iron are more complete, but the degree of dispersion of the segregation is high.

The samples annealed at 800° before the test were covered with a thick light film after a test of 250 hours. The microstructure of the samples shows a selective corrosion along the grain boundaries of the α -phase, where the segregated intermetallides are located. Redistribution of nickel either in the surface film or in the transition film or inside the sample was not shown. Samples treated otherwise had a dark tight surface film after 580 hours test. The autoradiograms of the unparallel cuts of these samples showed no redistribution of nickel in the surface film and inside the sample.

The distribution of iron in zirconium depends upon the heat treatment of the alloy. When annealing at 800° during 40 hours the distribution of iron is in the form of coarse intermetallides along the boundaries of coarse grained α -phase. After annealing at 1000° the iron is distributed along the subboundaries of the α -phase. Hardening at 1000° gives a uniform distribution of iron.

The samples annealed at 800° were covered with a white film after 125 hours. The samples after the heat treatment had a good surface condition during a test for 250 hours. No distribution of iron was observed on the surface film and in it during the corrosion process in samples annealed at 750° and 1000° and hardened at 1000° (fig.6). The microstructure of the transition layer of the samples does not show the selective corrosion of the alloy. In samples annealed at 800° a deeper corrosion of the grain boundaries in α -phase was observed. The segregated intermetallides were located along the boundaries (fig. 7a). The autoradiogram and the microstructure of the surface film are shown in fig. 7b. The iron is seen to be present in the oxide film.

Fig.8 shows autoradiograms of unparallel cuts of the samples of pure zirconium ("a"), of the zirconium alloy with nickel and iron ("b" and "c") and zirconium alloy with nitrogen ("d") after corrosion tests in tritium water. In all the cases we see that as a result of the corrosion of samples hydride inclusions are found.

In zirconium, containing 0.025% of nitrogen, the quantity of the hydride phase is much greater than in other two alloys, i.e. the presence of nitrogen in zirconium makes the metal more susceptible to hydrogen absorption during the corrosion process. In the alloy with nitrogen the hydrides are distributed along the boundaries and subboundaries of grains and form a characteristic grid.

In pure zirconium and in its alloy with iron and nickel after an equal length of test the quantity of hydrides and the character of their distribution are nearly the same and the hydrides are located as separate accumulations.

On the boundary between the metal and the oxide film there is no preferential location of hydrides i.e. there is no hydride sublayer under the oxide film. This was determined for all the investigated alloys under different test exposures.

The regions of the sample surfaces which on unparallel cuts are interstitial between the metal and oxide film were investigated. During the preparation of the unparallel cuts the oxide film could not be cut under the given angle (about 2°), but being brittle, cleaved, forming steps. Besides the oxide film itself had a certain relief. Therefore the boundary of the cleave of the oxide film was not straight. Some of the protruded places of the film cleaved forming closed areas, free of oxide film, and surrounded by the undestroyed film.

The left part of fig.10 shows one of such areas under side illumination; the right part of fig.10 shows the autoradiogram of the same area. One can clearly see that hydride formations are located in the centre of the area.

It is known that the volume increases about 20% with the formation of the zirconium hydride (I3). If such a large increase of the volume takes place directly under the oxide film it causes a local swelling of the film and this in its turn causes considerable stresses in it. When the stresses reach some critical value the film may crack in places of swelling. Thus the formation of hydride parts under the oxide film causes the decreasing of its protecting properties and promotes the increasing of the corrosion process in the water-vapour media. Such conclusion agrees with results of the work (I4).

Electron microscopic investigations of the oxide film on
zirconium and its alloys after corrosion

The electron microscopic investigation of the oxide film formed on zirconium and its alloys with tin, iron, nickel, niobium and chromium during the corrosion process was carried out for studying its structure. Fig. 10 shows some typical electron microphotos of the surface of zirconium samples and those of its alloys after their long corrosion in water-vapour media at 370 and 400° (a,b) and after a short time (3 sec.) oxidation in oxygen at 120 mm Hg and 1100°C (c). On these samples the film has a clearly visible structure of oxide grains and the substructure resembling a system of parallel lines. The size and the form of the oxide grains remain such as were those of the alloy crystals. The appearance of linear substructure in the grains of the oxide film is probably due to the plastic flows in the film induced by clamping stresses. These stresses appear in the film due to a great difference in metal and oxide volumes (the volume ratio of ZrO_2 and Zr is 1.6) and due to a very tight cohesion between the film and the metal.

The space between the lines in the substructure of single grains is approximately equal, but the direction of the lines is different in various grains; there are such grains where the linear substructure is absent. This proves that the generation of substructure lines is connected with the orientation of crystals of the oxide in the film.

The linear substructure of the oxide film on zirconium and its alloys is formed after a long corrosion in the steam-water media and after a short-time oxidation in oxygen at high temperatures (Fig. 10b).

The investigation of cross sections of the oxide films on zirconium and its alloys after a long corrosion proved the appearance of longitudinal fractures and lamination of the film observed in the paper (15). It was found that the appearance of longitudinal fractures is followed by the appearance of cross fractures, which pass not along the grain boundaries but across the grains themselves.

Conclusion

I. In the carbon alloys of zirconium during the corrosion process decarbonization of the oxide film takes place that probably is connected with the formation of carbon oxides and their

removal. Alloying of zirconium separately with tin, niobium and iron and nickel especially eliminates the decarbonization process slightly. The degree of decarbonization in separate films is different that probably is connected with anisotropic diffusion of oxygen into the lattice of α -zirconium. The selective corrosion along the boundaries and subboundaries of the grains is observed in zirconium alloy with 0.1 W per cent of carbon.

2. The corrosion resistance of zirconium alloys with iron and nickel depends on their previous heat treatment. The short times annealing, which leads to finely dispersed segregations of intermetallides along the boundaries and subboundaries, facilitates the greatest corrosion resistance. The long annealing leads to a great extension of grains and to almost complete segregation of intermetallides along the grain boundaries that in its turn leads to the decrease of corrosion resistance.

3. The presence of nitrogen in zirconium makes the metal more susceptible to hydrogen absorption during the corrosion process. In nitrogen alloys the hydrides locate along the boundaries and subboundaries of zirconium grains and make up a characteristic grid. In pure zirconium and its alloys with iron and nickel after corrosion under the same conditions the hydrides locate as single accumulations, the quantity and nature of hydride distribution being almost the same.

4. The hydride sublayer was not found at the boundary between the metal and the oxide film. The local appearance of the hydrides immediately under the oxide film followed by large volume changes leads to the fracturing of the oxide film and to the loss of its protective properties.

5. After a long corrosion (1000 hours and more) linear structure is observed in the grains of oxide film on zirconium and its alloys. This structure appears as a result of the plastic flow in the film which appears due to the great difference in metal and oxide volumes and due to a tight cohesion between the oxide film and the metal.

Table I

No	Alloy base	Alloying additions, W per cent					Heat treatment	Test temperature, °C	Time hours
		C	Sn	Fe	Ni	Nb			
I.	Zr	0.1 ^{*)}					Annealing 750°-1 hr Annealing 800°-40 hr Annealing 1000°-2 hr hardening at 1000° (after exposure for 2 hr)	370	125
2.	Zr	0.05 ^{*)}	1.0				annealing 750°-1 hr annealing 1000°-2hr	370	580
3.	Zr	0.1 ^{*)}	1.0				annealing 750°-1hr	400	125
4.	Zr	0.1 ^{*)}		0.8			annealing 750°-1hr	400	958
5.	Zr	0.1 ^{*)}			0.8		annealing 750°-1hr	400	836
6.	Zr	0.1 ^{*)}				1.0	annealing 750°-1hr	400	1045
7.	Zr				0.6 ^{*)}		annealing 750°-1hr annealing 1000°-2hr hardening at 1000° (after exposure for 2 hr)	370	125 250
8.	Zr			0.6	0.4 ^{*)}		annealing 750° } 1 hr annealing 800° } annealing 1000°-2hr hardening at 1000° (after exposure for 2 hr)	370	580 250 580
9.	Zr			0.5 ^{*)}			annealing 750° } 1hr annealing 800° } annealing 1000°-2hr hardening at 1000° (after the exposure for 2 hr)	400	580 250 125 250

*)Radioactive impurity

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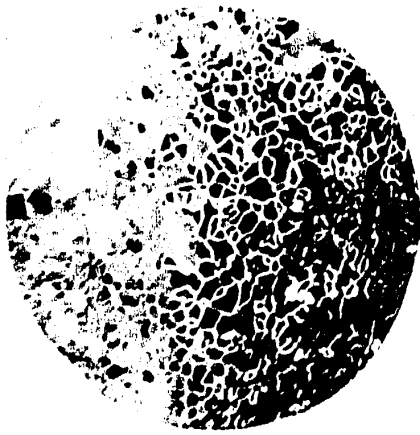


Fig. 1 (a)



Fig. 1 (b)

Fig.1. Autoradiogram of an unparallel cut and the microstructure of the transit layer of the zirconium alloy with 0.1% carbon annealed before the corrosion tests at 800°.



Fig.2. Autoradiogram of an unparallel cut of the zirconium alloy with 0.1% carbon annealed before corrosion tests at 1000°.

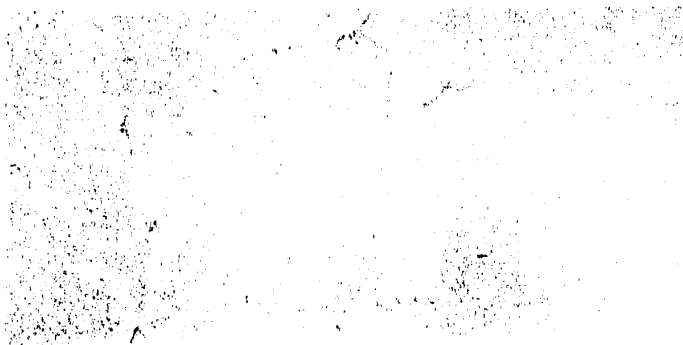


Fig. 3 (a)

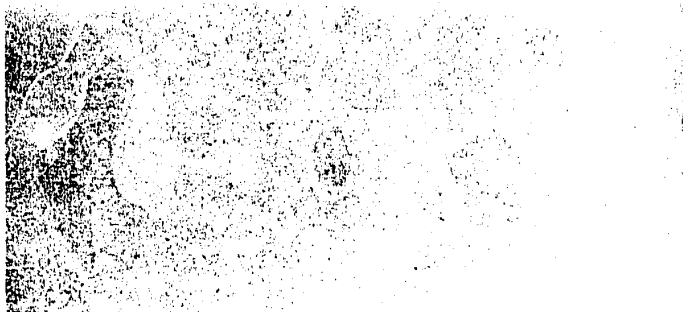


Fig. 3 (b)

Fig.3. Autoradiogram of the surface of the sample a) before and b) after the corrosion tests of the zirconium alloys with 0.1% carbon hardened at 1000° .



Fig.4. Autoradiogram a) of the unparallel cut and b) microstructure of the transit layer of the zirconium alloy with 0.6% nickel annealed before corrosion tests at 1000° .

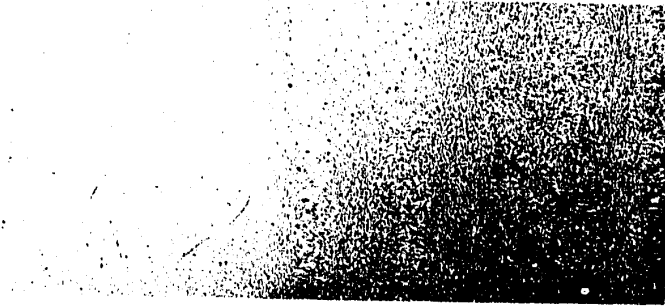


Fig. 5 (a)



Fig. 5 (b)

Fig. 5. Autoradiogram a) of the unparallel cut and b) the microstructure of the transit layer of the zirconium alloy with 0.6% nickel annealed before the corrosion tests at 750° .

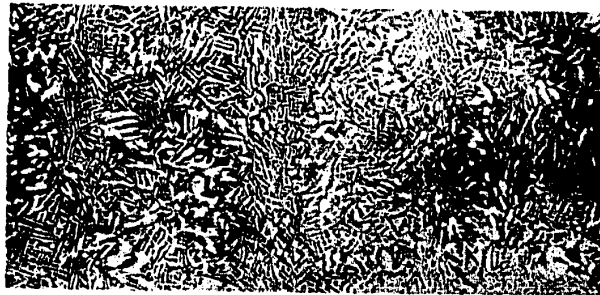


Fig. 6. Autoradiogram of an unparallel cut of the zirconium alloy with 0.5% iron, annealed before the corrosion tests at 1000° .

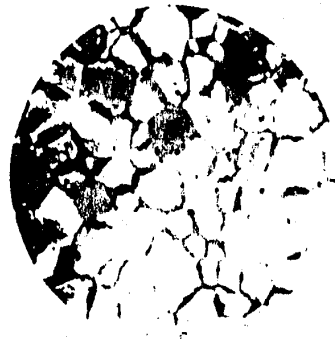


Fig. 7 (a)

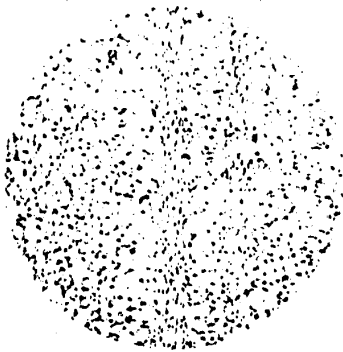


Fig. 7 (b)

Fig.7. Autoradiograms (left) and microstructures (right) of the surface film (b) and transitional layer (a) of the zirconium alloy with 0.5% iron annealed before corrosion tests at 1000°.

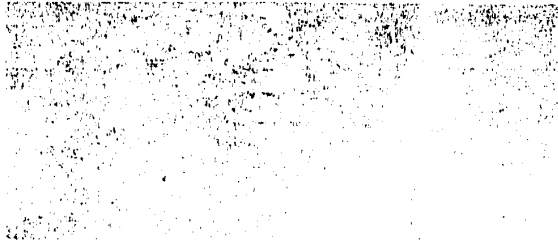


Fig. 8 (a)



Fig. 8 (b)

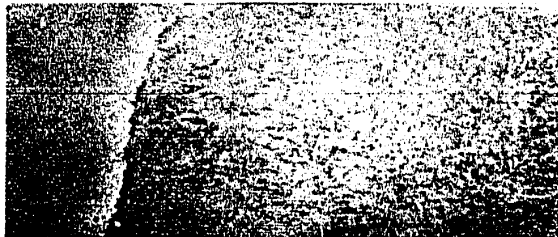


Fig. 8 (c)



Fig. 8 (d)

Fig.8. Autoradiograms of an unparallel cut of samples after tests in the vapour of tritium water:a) of pure zirconium after corrosion tests for 300 hours.b) of zirconium alloy with 0.7% iron and 0.7% nickel after corrosion tests for 300 hours. c) the same as given in b) after corrosion tests for 750 hours. d) of zirconium with 0.025% nitrogen after corrosion tests for 300 hours.



Fig. 9 .Microstructure (left) and autoradiogram (right) of the region under the oxide film taken away, where hydrides of zirconium are seen (600).

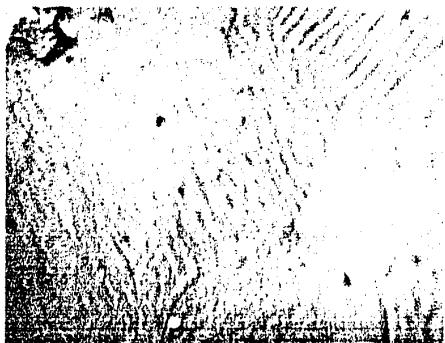


Fig. 10 (a)



Fig. 10 (b)



Fig. 10 (c)

Fig. 10. Electronic microphotoes of the surfaces of the samples after corrosion in water vapour medium at 370°C for 3400 hours (x8000): a) idodide zirconium. b) zirconium alloy with 1% niobium. c) zirconium alloy with 0.6% tin, 0.6% iron, 0.6% nickel, 1% niobium. d) zirconium alloy with 1% tin, 0.1% chromium. e) zirconium oxidised in oxygen at 1100°C for 3 sec.